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ORCHARD SPRAYS IN NEW ZEALAND.

I. THE SULPHUR SERIES.

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THIS is the first of a series of articles covering the orchard sprays in commercial use in New Zealand. The articles are based on information secured as the result of recent investigations conducted primarily to obtain data for framing the regulations necessary to make operative the Fungicides and Insecticides Act of 1927. The object of the present paper is to discuss the available types of sulphur, to indicate their respective values, the unit by which such values may be assessed, the manner in which sulphur acts as a fungicide, &c.

HOW SULPHUR ACTS AS A FUNGICIDE.

Although sulphur has been used as a fungicide since 1846 (in which year it was introduced in England to combat the mildew of grape-vines), it has only comparatively recently been introduced into orchard practice. In New Zealand it was first used about 1916 to combat powdery-mildew and black-spot of apple-trees, and more recently, alone or in the form of the so-called "dry mix," as a controllant of brown-rot and leaf-rust of stone fruits. Although this material has been in use for a longer period than any other spray, it must be admitted that even to-day the manner in which it acts is but imperfectly understood. Numerous theories have been published, and the fungicidal action of sulphur has been attributed to many compounds which it is capable of forming when combined with oxygen or hydrogen. Thus, writers have held that its toxicity was due to the production of gases such as sulphur dioxide or hydrogen sulphide; to the production of sulphurous, sulphuric, thio-sulphuric, or pentathionic acids; or due to the fact that it acted directly either in the form of finely divided particles or as sulphur vapour.

From a consideration of the experimental data presented it is probable that the following approximates to an accurate explanation of the toxicity of this element. It would appear that when sulphur is applied to a plant it gives off continuously either minute solid particles (Barker, 1928), or, what is more probable, a volatile gaseous sulphur (Goodwin and Martin, 1928; McCallan and Wilcoxon, 1931). This vapour (or these particles) is diffused through the air and deposited upon spores or hyphæ of fungi in the vicinity, as well as upon host-plant tissues, and there condensed to solid particles of sulphur. According to Goodwin and Martin (1929) it is these minute particles which are toxic to fungi to which they have been applied; but Barker (1928, 1930) and McCallan and Wilcoxon (1931) consider that these particles are converted into hydrogen sulphide, which acts as the toxic agent. Barker (1930) thought that conversion of these minute particles into hydrogen sulphide was effected upon the exterior of the fungus (or host plant) by means of a substance emerging from the tissues; whereas McCallan and

Wilcoxon (1931) held that conversion occurred within the tissues. In both reduction was considered to be of an enzymic nature. It has been convincingly shown by the experiments of Marsh (1928), Barker (1928, 1930), and McCallan and Wilcoxon (1931) that the gas hydrogen sulphide is toxic to fungi (and, in lesser degree, to the host-plant tissues) as was demonstrated first apparently by Pollacci (1875) upwards of half a century ago.

Factors affecting the Fungicidal Efficiency of Sulphur.

Recent investigations have shown that the fungicidal value of a sulphur may be measured by the size of the particles of which it is composed. Thus Young (1922), Wilcoxon and McCallan (1930), and Goodwin, Martin, and Salmon (1930) have shown that the toxicity of a sulphur is increased as the size of the sulphur particles is decreased. This may be due to the fact that the smaller the particles the greater the surface area, with a consequent increase in the quantities of sulphur vapour produced by a given amount of sulphur. There is also a definite correlation between the size of the sulphur particles and the quantity which remains upon fruit and foliage after application. For Fitch (1925) found that from 40 to 64 per cent. of a dusting sulphur was lost shortly after application; and Thatcher and Streeter (1925) showed that when a sublimed sulphur was applied from 89 to 94 per cent. was lost within one week of application. In this Laboratory it has been found that whereas the majority of the particles of a sublimed sulphur had disappeared from leaves sprayed four days previously (save those caught in leaf-hairs or lodged in crevices), leaves sprayed with a colloidal sulphur were found to be coated with a continuous film of particles, which were not dislodged when leaves were sectioned for examination. From an examination of leaves sprayed with different sulphurs it is evident that particles of a size in excess of 50 microns (this term will be explained below) fail to adhere to foliage for more than four days, the majority disappearing within a few hours of application.

The practical significance of this is that the smaller the particles the greater the amount of sulphur which will remain on a tree for a given time, permitting of a reduction in the quantities of the finer sulphurs that need be applied.

Efficacy of a sulphur may be affected by the degree of coverage secured; thus it is possible that the greater efficacy of a colloidal sulphur over a sublimed or ground sulphur is due to the fact that with the former a continuous film of particles is deposited over the leaf or fruit surfaces, whereas with the latter the particles, at normal dosages, are somewhat widely scattered.

The size of the particles likewise plays a part in the practical application of sulphur sprays. Mixed with water only the finest of sulphurs will remain in suspension for more than a brief period, the others requiring constant agitation to prevent the particles settling in the spray-tank. This is significant, as where stationary power plants are in operation there is danger of blockage of pipe-lines, where these are at all long, when coarse sulphurs are used.

Measurement of Sulphur Particles.

As has been shown, the value of a sulphur as a spray may be measured in terms of the size of the particles of which it is composed. For this purpose the following four methods have been used:—

(1) *Sieving.*—In the United States of America sulphurs are offered for sale on the basis of their being able to pass through certain sieves, 200- and 300-mesh sieves being regarded as standard for dusting and spraying purposes. Such sieves require that particles shall be of a theoretical size of not more than 74 microns for the 200 mesh, and about 47 microns for the 300 mesh. Actual measurements of samples of all commercial sulphurs on the New Zealand market have shown that the sizes of maximum particles range between 125 and 175 microns, quite 60 per cent. of the most finely ground being above 50 microns. It is evident therefore that there is little if any correlation between the sieve standards and the commercial materials offered on this market. Tests have shown that it is extremely difficult to pass even small quantities of a ground sulphur through a 200-mesh sieve, and practically impossible to use the finer series, which precludes the practical application of this method of measurement.

(2) *Chancel Test.*—In this a given quantity of sulphur (usually 5 grammes) is placed in a vessel, termed a Chancel tube, which is calibrated into one hundred divisions, each representing a "Chancel degree." To the tube is then added a given quantity of anhydrous ether. The mixture is then shaken and the sulphur allowed to settle, when its height in the tube is read in terms of degrees. The higher the reading the better the sulphur is supposed to be as a fungicide. Actual tests conducted in this Laboratory have shown that these Chancel degrees bear no relation to particle size, the best readings being secured with sulphurs in which the particles are aggregated into coarse groups. Consequently the process is worthless as a measure of the efficacy of sulphurs for spraying purposes.

(3) *Sedimentation Test.*—This is based on the assumption that particles of sulphur of different sizes have different periods of settlement.

The following method has been used in attempts to measure the relative fineness of colloidal sulphurs. Into glass cylinders are introduced measured quantities of the sulphurs, and equal amounts of water added to each. The vessels are then agitated until complete suspension has been secured, and are then placed side by side, and the contents allowed to settle, the rate of settlement of each being measured at periodic intervals. Success is possible only if no protective colloid is present (substances, such as glue, added in small quantity to hold particles in suspension for a prolonged period), for the presence of such in any sample would prevent measured results from being secured, and moreover would be difficult to detect by analysis. It is noteworthy that protective colloids are usually used during the preparation of these sulphurs.

We have recently applied this test in modified form to measure the relative percentages of coarse and fine particles of ground and

sublimed sulphurs. In this process (which is still in the experimental stage) a given quantity of sulphur is mixed with a measured volume of water to which has been added a small quantity of soap solution to act as a wettable agent. After being agitated until all material is in suspension, each vessel is placed upright and the particles allowed to settle for a given time, when the water (containing the finer particles of sulphur) is pipetted off and placed in a second container. The process is repeated, varying degrees of fineness of particles being secured by varying the times of sedimentation. The precipitates are then dried and the sulphur content obtained by weighing. The method has so far proved reasonably reliable, since particles of these types of sulphur are usually too large to be affected appreciably by any colloid which may be present in the suspension. By applying the method to a commercial ground sulphur we have ascertained that between 60 and 70 per cent. of the particles are of a size in excess of 50 microns; and with a commercial sublimed sulphur between 85 and 90 per cent. were found to be in excess of this figure.

(4) *Microscopic Measurement.*—The use of the microscope in determining the relative sizes of particles of sulphur has not yet become general, since it is only recently that the significance of particle size has been demonstrated. But consideration of the available processes has shown that this is the only means at hand whereby the size of the particles of all types of sulphurs on the market may be gauged with any degree of accuracy, so that it is probable that this method will play an important part in future analyses. After making a study of all sulphurs offered for sale in New Zealand, I believe that by the aid of the microscope it is possible to segregate these sulphurs into groups upon certain characteristics described below.

The microscope shows that sublimed and ground sulphurs exhibit a great range in particle size. As it is not possible to average these, measurements must of necessity be given in minimum and maximum figures. Further subdivision of the sizes of the particles may be undertaken, if required, by the sedimentation test. As the unit of microscopy is the micron (which equals $\frac{1}{1000}$ of 1 millimetre, or about $\frac{1}{25000}$ of 1 in.) all measurements herein are expressed upon this scale.

Classification of Sulphurs.

Microscopic analysis of the commercial sulphurs available shows that it is possible to group them under the following four headings:—

(1) *Ground Sulphur.*—This sulphur, sometimes termed flour sulphur, is prepared by mechanical grinding of refined roll or lump sulphur. The characteristics of such a sulphur, as defined herein, are that the particles are in the form of crystals with definite cleavage angles, and are pale yellow and translucent in transmitted light. Whatever their size, they remain distinct from one another, and do not become massed into groups. The particles exhibit great diversity of size (Fig. 1), the minimum being as low as 4 microns, and the maximum in the vicinity of from 125 to 250 microns, according to the grade of the sample.

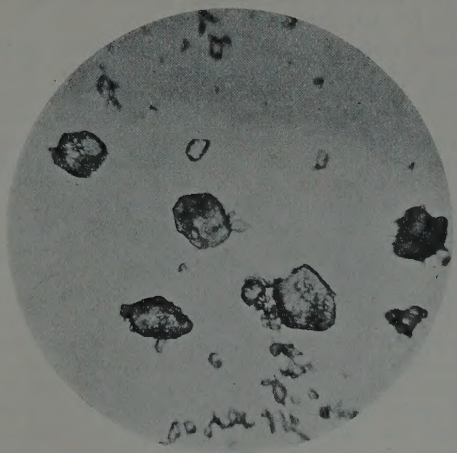

FIG. 1. PHOTOMICROGRAPH OF A GROUND SULPHUR. × 130.
Note crystalline nature of particles.

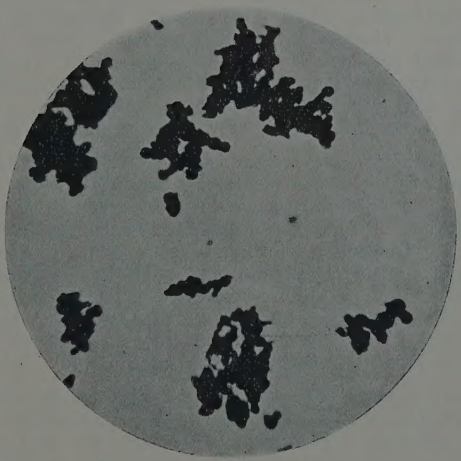

FIG. 2. PHOTOMICROGRAPH OF A SUBLIMED SULPHUR. × 130.
Note manner in which particles are agglutinated into masses.

[*Photomicrographs by W. D. Reid.*

Sulphurs of this type are usually applied at the rate of from 10 lb. to 12 lb. per 100 gallons of water.

(2) *Sublimed Sulphur.*—This material, commonly known as flowers of sulphur, is prepared by a process of sublimation. Sulphur or ore containing such is roasted in a furnace, and the vapour produced is led through flues into chambers where it is condensed by cooling and the sulphur deposited. Theoretically, such a sulphur is composed of rhomboid crystals, but in all commercial samples examined the particles were found to be more or less spheroidal, opaque, and firmly cemented into chains or irregular masses (Fig. 2). These aggregates vary greatly in size and shape, being from 150 to 400 microns across, and the particles of which they are composed when dissociated are between 8 and 30 microns. When such sulphurs are passed through a spray-pump, the masses do not break up to any appreciable extent, as has been demonstrated in this Laboratory by passing given quantities through a spray-pump (under a pressure of 100 lb.) on to sheets of paper, and examining these subsequently under the microscope. The fact that such a sulphur is largely composed of coarse particles, which precludes their remaining upon the leaf surface for any time, explains why sublimed sulphurs have proved relatively ineffective as controllants of black-spot and powdery-mildew in New Zealand.

Sublimed sulphurs are applied at rates comparable with ground sulphurs—namely, from 10 lb. to 12 lb. per 100 gallons.

(3) *Precipitated Sulphur.*—Under this heading are included certain sulphurs which occupy an intermediate position between the two just discussed and the colloidal series. Several have been offered for sale under the trade names of milk of sulphur, precipitated sulphur, or flotation sulphur. Their characteristics, as defined herein, are the size of the individual particles (2 to 12 microns), their crystalline translucent appearance, and the characteristic manner in which they tend to agglutinate into groups 200 microns or more across, which appear under the microscope not unlike snow or frost crystals (Fig. 3).

Sulphurs of this type are prepared by chemical precipitation, several methods being available, such as (*a*) by treating sodium thiosulphate with sodium bisulphate in the presence of glue; (*b*) by adding a saturated solution of sodium thiosulphate to concentrated sulphuric acid; or (*c*) by treating a solution of commercial lime-sulphur with sulphuric acid. Considerable confusion exists in literature as to the differences between these sulphurs and the colloidal series, as several prepared by chemical precipitation are called colloids. Materials prepared by the three processes mentioned are seen under the microscope to show the characteristic features of precipitants.

Precipitated sulphur has proved most disappointing when tested under field conditions, showing little if any improvement over ground or sublimed sulphurs. The probable reason for this is that the particles form aggregates which are too large to remain on the tree, since we have demonstrated that they are about 200 microns across and not broken up to any extent by passage through the spray-pump. This material is usually applied at between 6 lb. and 8 lb. per 100 gallons.

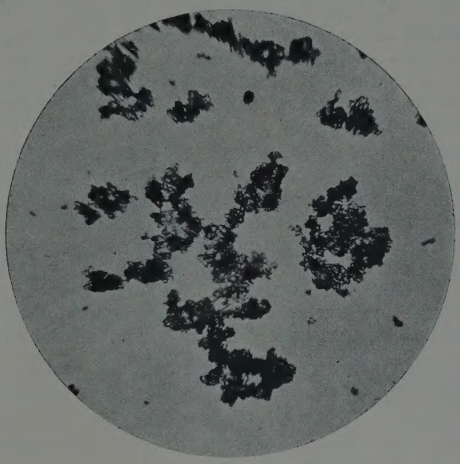

FIG. 3. PHOTOMICROGRAPH OF A PRECIPITATED SULPHUR. × 130.
Note crystalline particles agglutinated into masses.

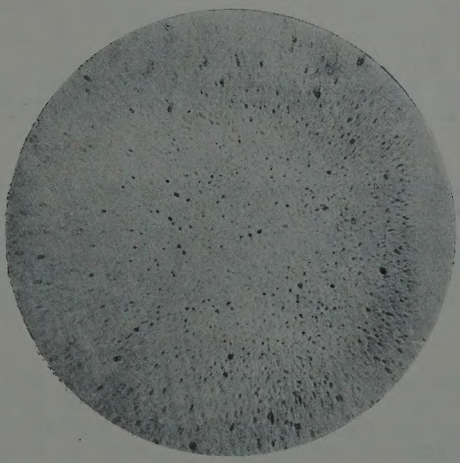

FIG. 4. PHOTOMICROGRAPH OF A COLLOIDAL SULPHUR. × 600.
Note the exceedingly fine particles and the manner in which they are dissociated. Only the larger particles are visible in this illustration.

[*Photomicrographs by W. D. Reid.*

(4) *Colloidal Sulphur.*—This name is applied to a group of sulphurs characterized in that the particles of which they are composed are mostly spheroidal in shape, of exceedingly fine dimensions, and do not aggregate, but remain dissociated (Fig. 4). The particles range in size from a small percentage of grains about 3 to 4 microns to ones so minute as to be beyond the limits of accurate measurement; the majority average between 0·5 and 1 micron.

This type of sulphur was introduced into the Dominion on a commercial scale only last season, but has been successfully used in Britain for the past three or four years, and is said to have largely displaced the coarser sulphurs in Europe. The name is rather unfortunate, since these materials are not colloids, but suspensions of minute particles of sulphur in water. The methods of preparation are trade secrets, and therefore not available; but it is probable they are prepared by electrical precipitation followed by grinding, in the presence of a protective colloid, in colloid mills of the Plauson type.

Colloidal sulphurs are recommended at from 2 lb. to 4 lb. per 100 gallons of water, on a basis of their containing 50 per cent. of sulphur in the concentrate.

The relative sizes of the particles of these four types of sulphurs may be summarized by the following table:—

Type of Sulphur.	Size of Particles.	
	Minimum.	Maximum.
	Microns.	Microns.
Ground*	4–8	125–250
Sublimed*	8–30	150–400
Precipitated	2–12	200
Colloidal	0·1†	4

* The maximum size of particles of these coarse sulphurs is governed by the grade of the sulphur under test, the figures given being secured from so-called 200- and 300-mesh samples.
† This figure is approximate, since it is not possible to measure accurately below about 0·25 micron.

Water Content.

Certain sulphurs are offered for sale in paste or fluid form. The advantage is that they can be mixed readily with water, but the disadvantage is that the sulphur content may vary in different brands, and thus upset the correct proportion of application. Consequently it is a matter of importance to the grower that he should know the water content of any brand, so that he may apply the recommended quantity of sulphur.

Wettable Agent.

As sulphur particles cannot be mixed readily with water it is customary to add to prepared spraying materials substances which will overcome this difficulty. Such treated sulphurs are known as wettable sulphurs. For this purpose any one of many substances (among which may be mentioned kaolin, calcium caseinate, glue, gelatine, soap, diatomaceous earth, hydrated lime, or alcoholic solutions of oleic acid) may be added to the sulphur in order to overcome the surface tension of the water sufficiently to enable a satisfactory suspension to be secured. As there is a possibility of reaction between

certain of these and other sprays with which the sulphur may be mixed, it is advisable to know the nature and percentage of the material used.

Uses of Sulphur Sprays.

In New Zealand sulphur sprays have been used since 1916 in the control of black-spot and powdery-mildew of apples, and since 1925 against brown-rot and leaf-rust of stone fruits. Until this last season only ground and sublimed sulphurs were used on a commercial scale, their use in recent years becoming general owing to a belief among orchardists that their addition to lime-sulphur tended to reduce the scorching and russetting effect of the latter on leaves and fruits. Precipitated sulphur was used to a lesser extent, since its high price and relative inefficiency compared it unfavourably with ground or sublimed sulphurs.

Experiments conducted in various parts of the Dominion during the past two seasons (particulars of which will be published at a later date) have shown that ground and sublimed sulphurs give partial control of black-spot, but have practically no effect upon powdery-mildew. Somewhat comparable results were secured with precipitated sulphur.

With colloidal sulphurs, on the other hand, outstanding results have been secured, for not only has this material (at 4–100) proved about equal to lime-sulphur as a controllant of black-spot, but it has given decidedly superior results in combating powdery-mildew. During the past season a commercial colloidal sulphur at the reduced strength of 2–100 gave almost complete control of powdery-mildew in one locality where lime-sulphur failed to hold it in check. The most outstanding results have been secured with a combination of colloidal sulphur and lime-sulphur (lime-sulphur 1–200 plus colloidal sulphur 2–100), this combination effectively controlling powdery-mildew, holding red-mite in check, and producing fruit noticeably free from russet.

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